

$\text{SrRuO}_3$        $\text{Ru, RuO}_2$   
 $\text{CaRuO}_3$

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(54) Abstract Title  
 Manufacturing a thin film by atomic layer deposition

(57) In a method of manufacturing a thin film a first reactant 11 is chemically absorbed on a substrate 3 by injecting the first reactant 11 into a chamber which the substrate is loaded. A physisorbed first reactant on the chemically absorbed first reactant is removed by purging or pumping the chamber. After the first reactant is densely chemically absorbed on the substrate by injecting the first reactant 11 into the chamber, the physisorbed first reactant on the dense chemisorbed first reactant is removed by purging or pumping the chamber. A second reactant 17 is chemically absorbed into the surface of the substrate by injecting the second reactant into the chamber. A physisorbed the second reactant on dense chemisorbed first reactant and the second reactant is removed by purging or pumping the chamber. A solid thin film is formed using a chemical exchange through densely absorbing the second reactant 17 on the substrate by again injecting the second reactant into the chamber. In this manner it is possible to obtain a precise stoichiometric thin film having a high film density, since the first reactant and the second reactant are densely absorbed and the impurities are completely removed by pumping or purging. The first and second reactants in a specific embodiment are respectively  $\text{Al}(\text{CH}_3)_3$  and water vapour. A whole range of films of elements, oxides or nitrides may be formed by this technique.

FIG. 10

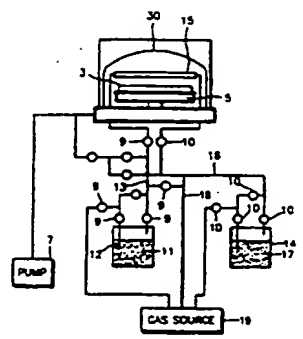
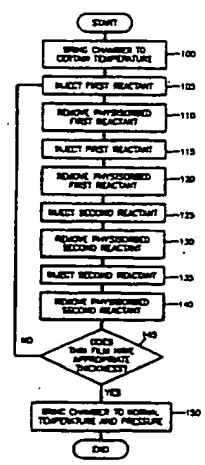


FIG. 11



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FIG. 1

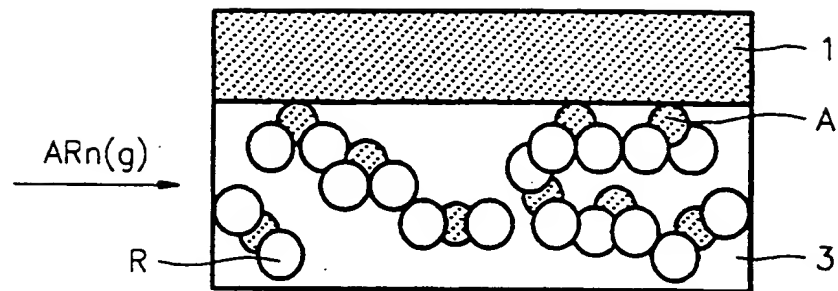


FIG. 2

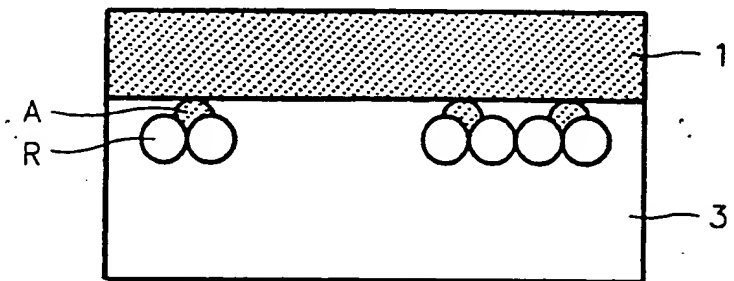


FIG. 3

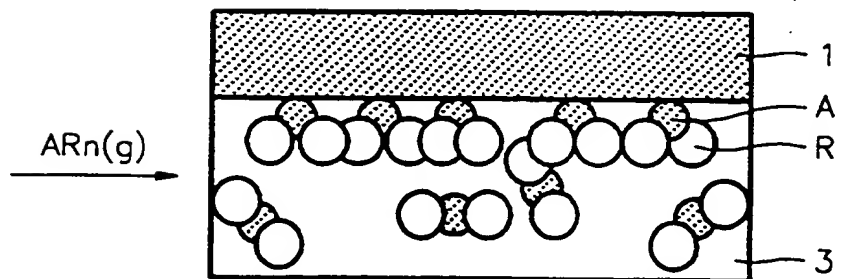


FIG. 4

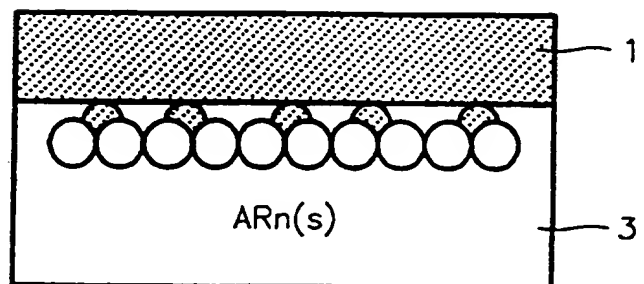


FIG. 5

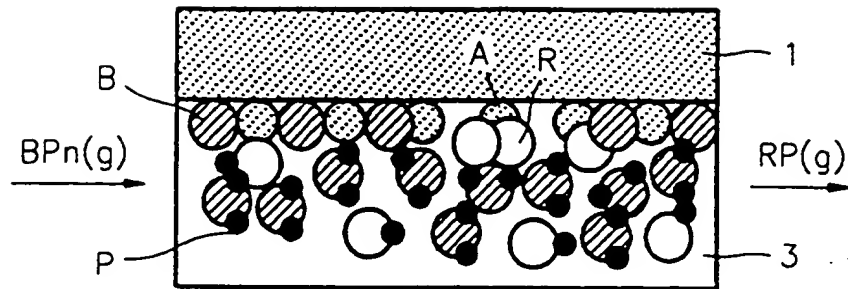


FIG. 6

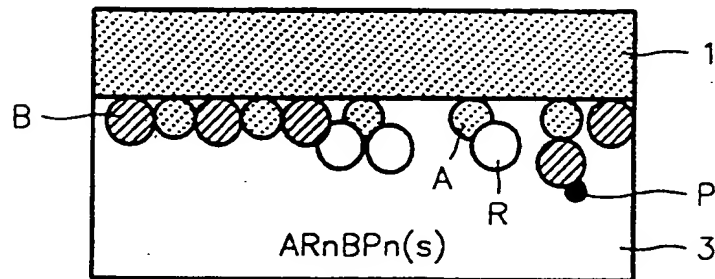


FIG. 7

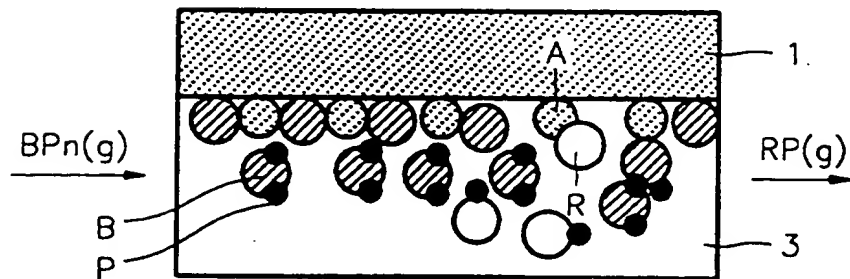


FIG. 8

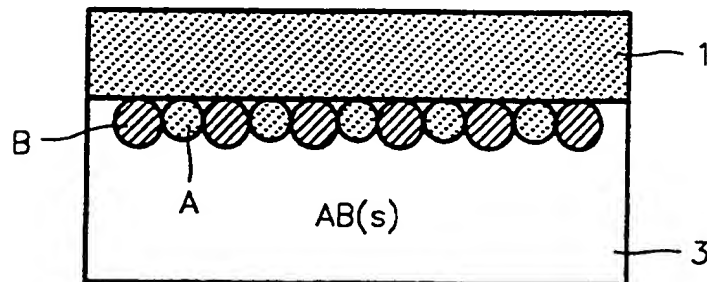


FIG. 9A

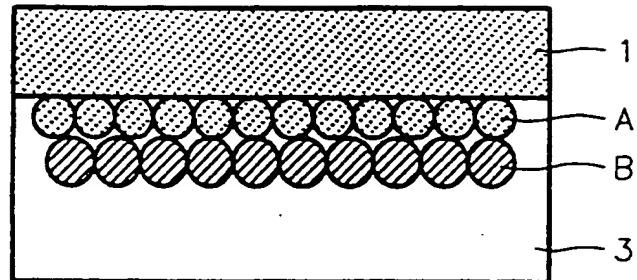
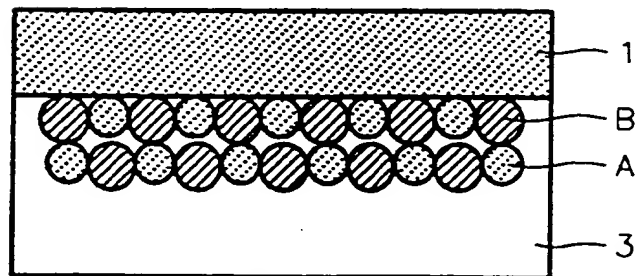


FIG. 9B



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FIG. 10

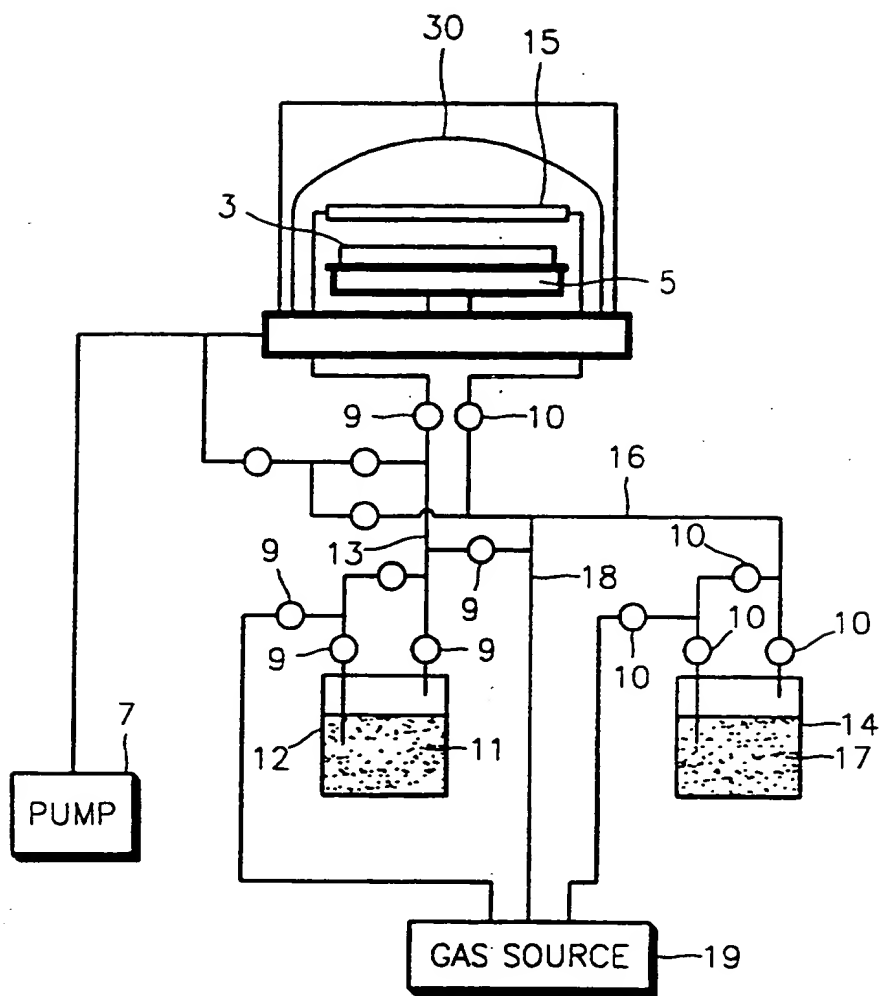
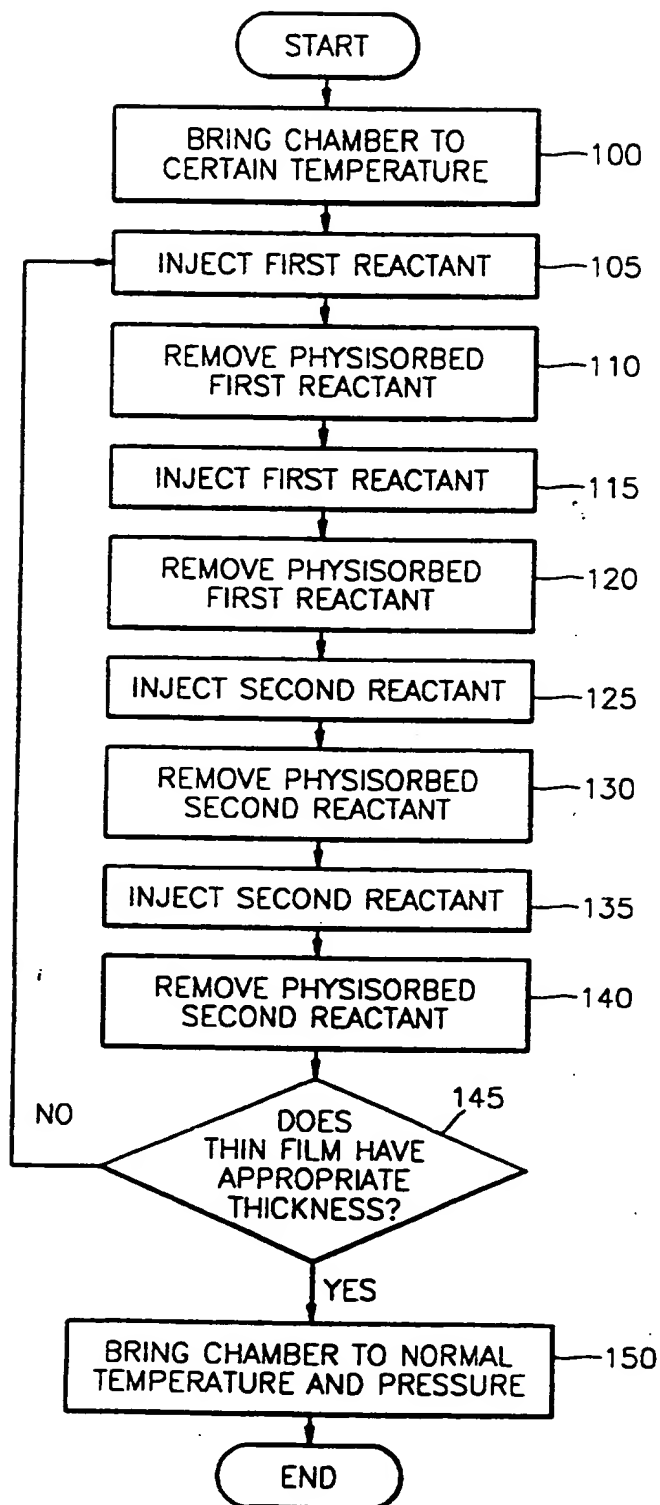


FIG. 11



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FIG. 12

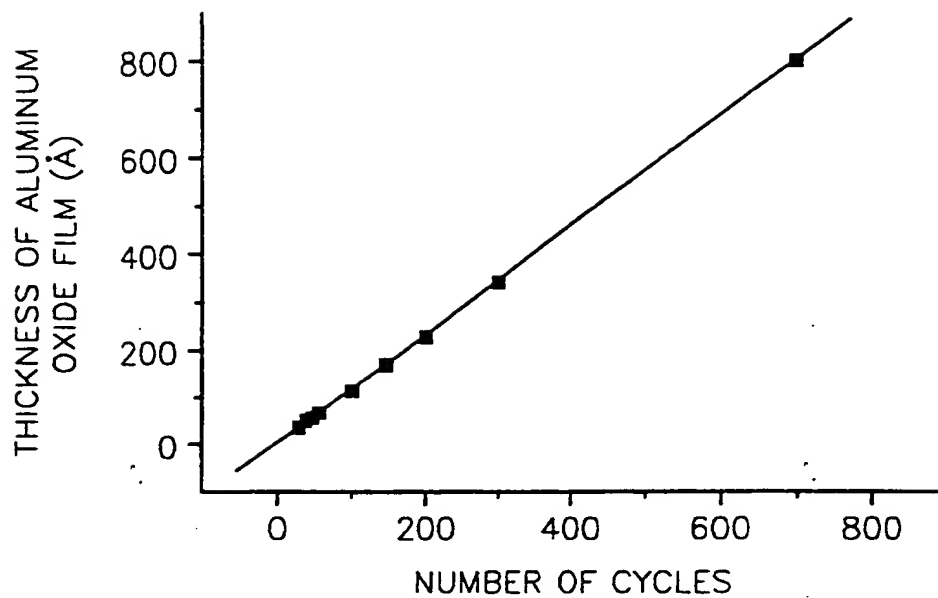


FIG. 13

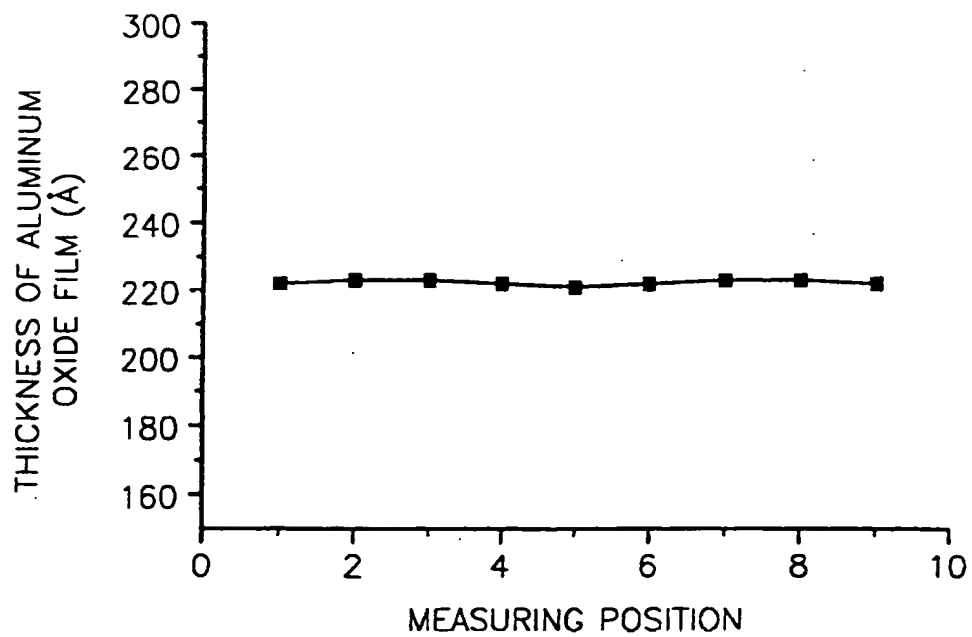


FIG. 14

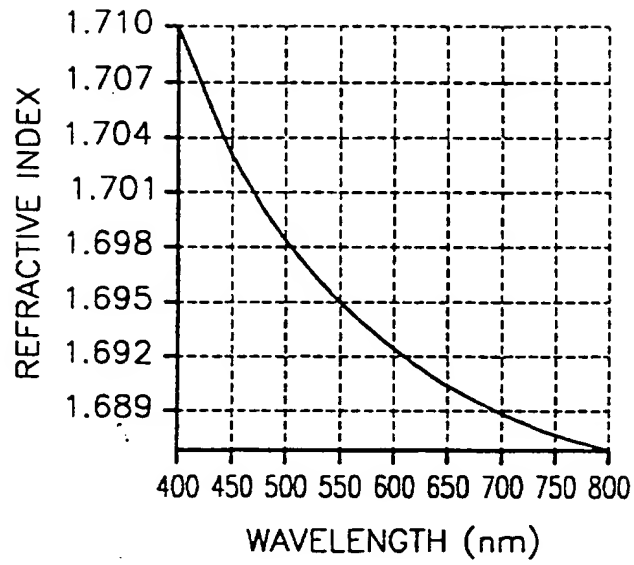
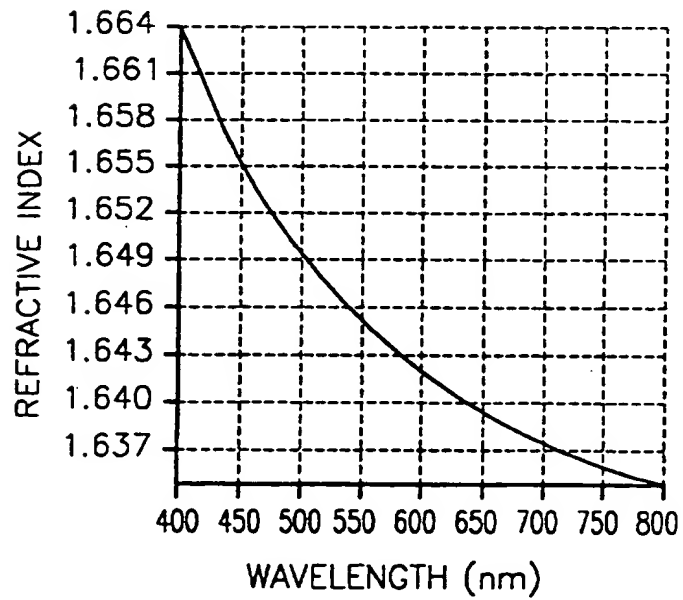


FIG. 15 (PRIOR ART)





## A METHOD FOR MANUFACTURING A THIN FILM

The present invention relates to a method for manufacturing a thin film, and more particularly, to a method for manufacturing a thin film by atomic layer deposition (ALD).

5 A thin film is typically used for a dielectric of a semiconductor device, a transparent conductor of a liquid-crystal display, or a protective layer of an electroluminescent thin film display. The thin film is formed through evaporation, chemical vapor deposition or by an ALD method.

10 ALD is a surface controlled process, and uses two dimensional layer by layer deposition. The deposition is performed in a surface kinetic regime so that the step coverage is excellent. Also, a reactant is decomposed through chemical exchange by periodically supplying the reactant without pyrolysis so that the resultant film has high density and precise stoichiometry. Also, the by-products caused by the chemical exchange is a gas which can be easily removed, so a chamber can be easily cleaned.  
15 The temperature is the only process variable in the ALD method, so the process is easily controlled and maintained.

However, in the conventional ALD, when insufficient reactant is absorbed on the surface of a substrate, a defect such as a pinhole is generated in the thin film. Therefore, the physical characteristics of the thin film, such as the film density, deteriorate. Also, in the conventional ALD, since a chemical ligand is not completely removed, it is not possible to obtain a precise stoichiometric thin film.  
20

According to the present invention, a method of manufacturing a thin film comprises the steps of:

- 25 (a) chemically absorbing a first reactant on a substrate by injecting the first reactant into a chamber which the substrate is loaded;  
(b) removing a physisorbed first reactant on the chemically absorbed first reactant by purging or pumping the chamber;

- (c) densely chemically absorbing the first reactant on the substrate by injecting the first reactant into the chamber;
- (d) removing the physisorbed first reactant on the dense chemisorbed first reactant by purging or pumping the chamber;
- 5 (e) chemically absorbing a second reactant into the surface of the substrate by injecting the second reactant into the chamber;
- (f) removing physisorbed the second reactant on the dense chemisorbed first reactant and the second reactant by purging or pumping the chamber; and,
- 10 (g) forming a solid thin film using a chemical exchange through densely absorbing the second reactant on the substrate by again injecting the second reactant into the chamber.

After densely absorbing the second reactant, the physically absorbed second reactant and residuals generated during the chemical exchange can be removed by purging or pumping the chamber. The processes of injecting the second reactant and removing

15 the physically absorbed second reactant and the residuals can be sequentially repeated two or more times. The processes of injecting the first reactant and removing the physically absorbed first reactant can be sequentially repeated two or more times. The substrate is (100) silicon substrate. The first reactant and the second reactant are comprised of an atom and a chemical ligand for constructing the solid thin film.

20 The solid thin film is comprised of one selected from the group consisting of a single atom thin film, a single atom oxide, a composite oxide, a single atom nitride, and a composite nitride. The single atom thin film is one selected from the group consisting of Mo, Al, Cu, Ti, Ta, Pt, Ru, Rh, Ir, W, and Ag. The single atom oxide is one selected from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{CeO}_2$ ,

25  $\text{Y}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $\text{RuO}_2$ , and  $\text{IrO}_2$ . The composite oxide is one selected from the group consisting of  $\text{SrTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{SrRuO}_3$ ,  $\text{CaRuO}_3$ ,  $(\text{Ba},\text{Sr})\text{TiO}_3$ ,  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ,  $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ ,  $(\text{Sr},\text{Ca})\text{RuO}_3$ ,  $\text{In}_2\text{O}_3$  doped with Sn,  $\text{In}_2\text{O}_3$  doped with Fe, and  $\text{In}_2\text{O}_3$  doped with Zr. The single atom nitride is one selected from the group consisting of SiN, NbN, ZrN, TaN,  $\text{Y}_3\text{N}_5$ , AlN, GaN, WN, and BN. The composite nitride is one

30 selected from the group consisting of WBN, WSiN, TiSiN, TaSiN, AlSiN, and AlTiN.:

In the present invention, it is possible to obtain a precise stoichiometric thin film having a high film density, since the first reactant and the second reactant are closely absorbed and the impurities are completely removed by pumping or purging.

Examples of the present invention will now be described in detail with reference to the accompanying drawings, in which:

FIGs. 1 through 8 describe processes of manufacturing a thin film using an atomic layer deposition according to the present invention;

FIGs. 9A and 9B show examples in which the thin film is manufactured using atomic layer deposition in different ways from that of the thin film of FIG. 8;

FIG. 10 is a schematic diagram of a thin film manufacturing apparatus used for a thin film manufacturing method according to the present invention;

FIG. 11 is a flowchart describing the thin film manufacturing method according to the present invention;

FIG. 12 is a graph showing the thickness of an aluminum oxide film per cycle manufactured by the thin film manufacturing method according to the present invention;

FIG. 13 is a graph showing uniformity in a substrate of the aluminum oxide film manufactured by the thin film manufacturing method according to the present invention; and

FIGs. 14 and 15 are graphs showing refractive index for wavelength of aluminum oxide films manufactured according to the present invention and a conventional method, respectively.

FIGs. 1 through 8 show a processes of manufacturing a thin film using atomic layer deposition according to the present invention. In FIGs. 1 through 8, when the thin film to be deposited is a two component compound comprised of A and B, a first reactant and a second reactant are respectively called  $AR_n(g)$  and  $BP_n(g)$ . Here,  $R_n$  is a chemical ligand formed of  $n$  R radicals.  $P_n$  is a chemical ligand formed of  $n$  P radicals. Here, (g) denotes a gas state.

Referring to FIG. 1, the first reactant is chemically absorbed (chemisorbed) and physically absorbed (physisorbed) into the surface of a substrate 1, for example, a (100) silicon substrate, by injecting the first reactant  $AR_n(g)$  into a chamber (not

shown) into which the substrate 1 is loaded. The first reactant is chemically absorbed into the surface of the substrate. The first reactant absorbed into the chemisorbed first reactant is physically absorbed. Since the first reactant  $ARn(g)$  was injected at one time, a space which can cause a chemisorption is covered with the physisorbed  $ARn(g)$ .  
5 Accordingly, an empty space 3 is formed on the substrate.

Referring to FIG. 2, the physisorbed first reactant is completely removed by purging or pumping the chamber in which the chemisorbed and physisorbed first reactant is formed. By doing so, the chemisorbed first reactant remains on the surface of the substrate 1. The chemisorbed first reactant is  $ARn(s)$  of solid state, and many parts  
10 of the surface of the substrate 1 are exposed. Here, (s) denotes a solid state.

Referring to FIG. 3, the first reactant is densely chemisorbed and physisorbed into the surface of the substrate 1 by again injecting the first reactant  $ARn(g)$  into the chamber including the substrate 1 on which the solid  $ARn(s)$  is formed. By doing so, the first reactant is chemisorbed and physisorbed into the empty space 3 shown in FIG. 1. Like  
15 in FIG. 1, the first reactant is chemisorbed into the surface of the substrate 1. The physisorbed first reactant is formed on the chemisorbed first reactant.

Referring to FIG. 4, the physisorbed first reactant is completely removed by pumping or purging the chamber including the substrate 1 on which the chemisorbed first reactant is formed. The process of injecting the first reactant and removing the  
20 physisorbed first reactant is performed twice, so only the densely chemisorbed first reactant, i.e., the solid  $ARn(s)$ , remains on the surface of the substrate 1 and impurities such as a chemical ligand are completely removed. Here, s denotes a solid state. In this example, the processes shown in FIGs. 1 through 4 can be repeated more than two times.

Referring to FIG. 5, a second reactant  $BPn(g)$  is injected into the chamber including the substrate 1 on which the densely chemisorbed first reactant is formed, and is chemically absorbed (chemisorbed) and physically absorbed (physisorbed). The second reactant absorbed on the surface of the substrate is chemisorbed. The second reactant  
25 absorbed into the chemisorbed second reactant is physisorbed. By doing so, the

chemisorbed first and second reactants form a monolayer which is not dense in levels of an atomic layer formed of A and B atoms by a chemical exchange. At this time, Rn and Pn, which are chemical ligands, are removed in a state in which a vapor pressure is high. Since the second reactant of FIG. 5 is not densely chemisorbed into the surface of the substrate like the first reactant of FIG. 1, the second reactant is inadequately chemically exchanged with the first reactant. Thus, impurities are generated in the monolayer, or a stoichiometric composition ratio is not met, since the second reactant is inadequately chemically exchanged with the first reactant.

Referring to FIG. 6, the physisorbed second reactant is removed by pumping or purging the chamber in which the monolayer which is not dense and the physisorbed second reactant are formed. By doing so, a solid monolayer which is chemisorbed is formed on the surface of the substrate. Since the solid monolayer of FIG. 6 is ARnBPn(s), impurities of RnPn(s) remain, the stoichiometric composition ratio is not met, and the film density is poor. Here, (s) denotes a solid state.

Referring to FIG. 7, in order to improve the above-mentioned stoichiometric composition ratio and the film density, the second reactant is chemically and physically absorbed into the surface of the substrate by again injecting the second reactant BPn(g) into the chamber including the substrate on which a solid monolayer which is not dense is formed. The second reactant absorbed into the surface of the substrate is chemically absorbed. The second reactant absorbed into the chemisorbed second reactant is physically absorbed. By doing so, the chemisorbed first and second reactants form a dense monolayer having a thickness of the levels of the atomic layer formed of the A and B atoms by the chemical exchange method. At this time, Rn and Pn, which are chemical ligands, are removed in a gas state having a high vapor pressure.

Since the second reactant of FIG. 7 is chemically absorbed into the surface of the substrate which is not densely chemisorbed in FIG. 5, the second reactant is sufficiently chemically exchanged with the dense first reactant, thus reducing the impurities in the single layer and meeting the stoichiometric composition ratio.

Referring to FIG. 8, the physisorbed second reactant is completely removed by purging or pumping the chamber in which the dense monolayer and the physisorbed second reactant are formed. By doing so, only the solid dense monolayer which is densely and chemically absorbed, i.e., AB(s), remains on the surface of the substrate. Here, (s) denotes a solid state. In this example, the processes of FIGs. 5 through 8 can be repeated more than two times.

In FIG. 8, A and B are formed on the surface of the substrate, thus forming a compound, AB(s). However, when the atomic layer deposition according to the present invention is applied, A may be formed on the surface of the substrate and B formed on A, thus forming the compound AB(s) as shown in FIG. 9A, or A and B may be formed on the surface of the substrate and B and A formed on A and B, thus entirely forming the compound AB(s).

FIG. 10 is a schematic diagram of a thin film manufacturing apparatus used for the thin film manufacturing method according to the present invention. FIG. 11 is a flowchart describing the thin film manufacturing method according to the present invention.

After loading a substrate 3, for example, a (100) silicon substrate into a chamber 30, the substrate is brought to a temperature of about 150°C to 375°C, preferably 300°C, using a heater 5 (step 100). At this time, the temperature of the heater 5 is maintained at about 450°C in order to maintain the temperature of the substrate at 300°C.

A first reactant 11 such as  $\text{Al}(\text{CH}_3)_3$  (TMA) in a first bubbler 12 is injected into the chamber 30 for 0.1 through 10 seconds, preferably, 0.5 second, while the chamber 30 is maintained at 150°C to 375°C (step 105).

Here, the first reactant 11 is injected using a bubbling method. The first reactant 11 is injected through a first gas line 13 and a shower head 15 by selectively operating a valve 9, after changing the first reactant 11 from a liquid state into a gas by injecting 100sccm of Ar carrier gas from a gas source 19 into the first bubbler 12 maintained at a temperature of 20 through 22°C. 400sccm of nitrogen gas from the gas source 19 is injected through a second gas line 18 and the shower head 15 in order to improve

the flow velocity of the first reactant 11 and dilute the first reactant 11 during the injection of the first reactant 11. As a result, 500sccm of gas provided to the chamber 30 during the injection of the first reactant 11. At this time, the pressure of the chamber is maintained at 1 to 2 Torr (133 to 266 Nm<sup>-2</sup>). By doing so, the first reactant 11 is chemisorbed into the surface of the substrate 3 to an atomic level. The physisorbed first reactant 11 is formed on the chemisorbed first reactant 11.

The physisorbed first reactant is removed by selectively operating the valve 9 to the chamber 1 while maintaining the temperature at 150 to 375°C and the pressure at 1 to 2 Torr (133 to 266 Nm<sup>-2</sup>), and purging the 400sccm of nitrogen gas of the gas source 19 for 0.1 through 10 seconds, preferably, 1 second, using the first gas line 13 or the second gas line 18 (step 110). In the present embodiment, the physisorbed first reactant is removed by purging. However, the physically absorbed first reactant can be removed by pumping the chamber to a vacuum state without purging.

The first reactant 11 is again injected into the chamber 30 from which the physisorbed first reactant was removed, like in the step 105 (step 115). At this time, the time spent injecting the first reactant in the step 115 is equal to or shorter than that spent injecting the first reactant in the step 105. The physisorbed first reactant is removed from the chamber 30, like in the step 110 (step 120). At this time, the time spent removing the physically absorbed first reactant in the step 120 is equal to or shorter than that spent removing the first reactant in the step 110. When the injection of the first reactant and the first purge process are repeatedly performed, the dense chemisorbed first reactant is formed on the substrate. In this example, the processes of injecting the first reactant and removing the physisorbed first reactant are each performed twice. However, the processes can be performed more times.

A second reactant 17 such as deionized water in a second bubbler 14 is injected into the chamber including the substrate on which the dense chemisorbed first reactant is formed, through the gas line 16 and the shower head 15 for millisecond to 10 seconds, preferably 0.5 seconds, by selectively operating a valve 10 while a temperature of 150 to 375°C and a pressure of 1 to 2 Torr (133 to 266 Nm<sup>-2</sup>) are maintained (step 125).

Here, the second reactant 17 is injected using the bubbling method, like the first reactant. Namely, the second reactant is injected through a third gas line 16 and the shower head 15 after changing the second reactant 17 from a liquid state to a gas state by injecting 100sccm of Ar carrier gas of the gas source 19 into the second bubbler 14 maintained at a temperature of 20 to 22°C. The 400sccm of nitrogen gas is injected through the second gas line 18 and the shower head 15 in order to improve the flow velocity of the second reactant 17 and to dilute the second reactant 17 during injection of the second reactant 17. As a result, the amount of gas provided to the chamber 30 during the injection of the second reactant 17 is 500sccm. At this time, the pressure of the chamber 30 is maintained at 1 to 2 Torr (133 to 266 Nm<sup>-2</sup>). By doing so, the second reactant is chemisorbed into the substrate 3 on which the dense chemisorbed first reactant is formed. The second reactant is physisorbed into the chemisorbed first and second reactants. An aluminum oxide film which is not dense in levels of an atomic layer is formed from the densely chemisorbed first reactant and the chemisorbed second reactant which is not dense, by the chemical exchange method.

The physisorbed second reactant is removed by selectively operating the valve 10 to the chamber 1 in which the aluminum oxide film which is not dense in the levels of the atomic layer is formed, and purging 400sccm of nitrogen gas of the gas source 19 for 0.1 to 10 seconds, preferably 1 second, using the second gas line 18 or the third gas line 16, while a temperature of 150 to 375°C and a pressure of 1 to 2 Torr (133 to 266 Nm<sup>-2</sup>) are maintained (step 130). In this example, the physisorbed second reactant is removed by purging. However, the physisorbed second reactant can be removed by pumping the chamber to a vacuum state without purging.

The second reactant 11 is again injected into the chamber 30 removed of the physisorbed second reactant, like in the step 125 (step 135). At this time, the time spent injecting the second reactant in the step 135 is equal to or shorter than that spent injecting the second reactant in the step 125. The physisorbed second reactant is removed from the chamber 30 like in the step 130 (step 140). When the processes of injecting the second reactant and removing the physisorbed second reactant are repeatedly performed, the densely chemisorbed second reactant on the substrate is formed. As a result, the dense chemisorbed first reactant and the dense chemisorbed



second reactant form a dense aluminum oxide film in levels of the atomic layer by chemical exchange. In this example, the processes of injecting the second reactant and removing the physisorbed second reactant are each performed twice. However, the processes can be performed more times.

5 Then, it is checked whether a thin film having a thickness of about 10 to 1,000Å is formed by periodically and repeatedly performing steps 105 through 140 (step 145). When the thin film has an appropriate thickness, the thin film manufacturing processes are completed by returning the temperature and the pressure of the chamber to normal and not repeating the above cycle (step 150).

10 In FIG. 11, the first and second reactants form the aluminum oxide film  $\text{Al}_2\text{O}_3$  using  $\text{Al}(\text{CH}_3)_3$  (TMA) and the deionized water. A TiN film can be formed if the first and second reactants are  $\text{TiCl}_4$  and  $\text{NH}_3$ . An Mo film can be formed if the first and second reactants are  $\text{MoCl}_5$  and  $\text{H}_2$ , respectively.

15 In the present invention, a solid thin film of a single atom, a single atom oxide, a composite oxide, a single atom nitride, or a composite nitride can be formed instead of the aluminum oxide film, the TiN film, and the Mo film. Al, Cu, Ti, Ta, Pt, Ru, Rh, Ir, W, and Ag can be used as the solid thin film of the single atom.  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $\text{RuO}_2$ , and  $\text{IrO}_2$  can be used as the single atom oxide.  $\text{SrTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{SrRuO}_3$ ,  $\text{CaRuO}_3$ ,  $(\text{Ba},\text{Sr})\text{TiO}_3$ ,  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ,  $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ ,  $(\text{Sr},\text{Ca})\text{RuO}_3$ ,  $\text{In}_2\text{O}_3$  doped with Sn,  $\text{In}_2\text{O}_3$  doped with Fe, and  $\text{In}_2\text{O}_3$  doped with Zr can be used the composite oxide film. Also,  $\text{SiN}$ ,  $\text{NbN}$ ,  $\text{ZrN}$ ,  $\text{TaN}$ ,  $\text{Y}_3\text{N}_5$ ,  $\text{AlN}$ ,  $\text{GaN}$ ,  $\text{WN}$ , and  $\text{BN}$  can be used as the single atom nitride.  $\text{WBN}$ ,  $\text{WSiN}$ ,  $\text{TiSiN}$ ,  $\text{TaSiN}$ ,  $\text{AlSiN}$ , and  $\text{AlTiN}$  can be used as the composite nitride.

20 As mentioned above, in the thin film manufacturing method of the present invention, after repeatedly injecting the first reactant and removing the physisorbed first reactant while the temperature and the pressure are uniformly maintained, the second reactant is repeatedly injected and the physisorbed second reactant is repeatedly removed. By doing so, it is possible to obtain a precise stoichiometric thin film having a high film

density, since the first reactant reacts with the densely deposited second reactant by chemical exchange, while the first reactant is densely deposited on the substrate.

FIG. 12 is a graph showing the thickness of the aluminum oxide film per cycle manufactured by the thin film manufacturing method according to the present invention.

5 The X axis denotes the number of cycles. Here, one cycle includes the steps of injecting the first reactant, removing the physisorbed first reactant, injecting the first reactant, removing the physisorbed first reactant, injecting the second reactant, removing the physisorbed second reactant, injecting the second reactant, and removing the physisorbed second reactant. The Y axis denotes the thickness of the aluminum oxide film. As shown in FIG. 12, in present invention, the aluminum is grown at a  
10 thickness of 1.1Å per cycle. This is similar to a theoretical value.

FIG. 13 is a graph showing the uniformity of the substrate of the aluminum oxide film manufactured by the thin film manufacturing method according to the present invention.

15 The X axis denotes the position at which the film thickness on an 8 inch (20.32cm) substrate was measured. The measurement positions were the center, four points spaced at 90° intervals around a circle concentric with the wafer's center and having a 3.5 inch (8.89 cm) radius, and four points spaced at 90° intervals around a circle concentric with the wafer's center and having a 1.75 inch (4.44 cm) radius. The Y axis denotes the thickness of the aluminum oxide film. As shown in FIG. 12, the  
20 uniformity is excellent over the 8 inch (20.32 cm) substrate.

FIGs. 14 and 15 are graphs showing refractive index according to wavelength of the aluminum oxide film manufactured by the present invention and a conventional method, respectively. The X axis denotes the wavelength of 400 through 800nm. The Y axis denotes the refractive index.

25 The refractive index of the aluminum oxide film manufactured by the present invention is 1.67 to 1.73 in the range of 400 to 800nm. In particular, as shown in FIGs. 14 and 15, at the wavelength of 500nm, the refractive index of the aluminum oxide

5 manufactured by the present invention is 1.698, which is larger than the refractive index 1.649 of the aluminum oxide manufactured by a conventional method. Accordingly, it is noted that the film density is high. Also, the refractive index of the aluminum oxide film manufactured by the present invention is similar to that measured after annealing the aluminum oxide film manufactured by the conventional method at 850°C for 30 minutes. Therefore, the aluminum oxide film need not be annealed.

## CLAIMS:

1. A method of manufacturing a thin film, comprising the steps of:
  - (a) chemically absorbing a first reactant on a substrate by injecting the first reactant into a chamber in which the substrate is loaded;
  - 5 (b) removing a physisorbed first reactant on the chemically absorbed first reactant by purging or pumping the chamber;
  - (c) densely chemically absorbing the first reactant on the substrate by injecting the first reactant into the chamber;
  - 10 (d) removing the physisorbed first reactant on the dense chemisorbed first reactant by purging or pumping the chamber;
  - (e) chemically absorbing a second reactant into the surface of the substrate by injecting the second reactant into the chamber;
  - (f) removing physisorbed the second reactant on the dense chemisorbed first reactant and the second reactant by purging or pumping the chamber; and,
  - 15 (g) forming a solid thin film using a chemical exchange through densely absorbing the second reactant on the substrate by again injecting the second reactant into the chamber.
2. A method according to claim 1, further comprising the step (h) of removing the physically absorbed second reactant and residuals generated during the chemical  
20 exchange in the step (g), by purging or pumping the chamber.
3. A method according to claim 2, in which each of the processes of injecting the second reactant and removing the physically absorbed second reactant and the residuals of the steps (e), (f), (g), and (h) are sequentially repeated two or more times.
4. A method according to any preceding claim, in which each of the processes of  
25 injecting the first reactant and removing the physically absorbed first reactant of the steps (a), (b), (c), and (d) steps are sequentially repeated two or more times.

5. A method according to any preceding claim, in which the time spent on injecting the first reactant in the step (c) is equal to or shorter than that spent injecting the first reactant in the step (a).
- 5 6. A method according to any preceding claim, in which the time spent injecting the second reactant in the step (g) is equal to or shorter than that spent injecting the second reactant in the step (e).
7. A method according to any preceding claim, in which the substrate is (100) silicon substrate.
- 10 8. A method according to any preceding claim, in which the first reactant and the second reactant are comprised of an atom and a chemical ligand for constructing the solid thin film.
9. A method according to any preceding claim, in which the solid thin film is comprised of one selected from the group consisting of a single atom thin film, a single atom oxide, a composite oxide, a single atom nitride, and a composite nitride.
- 15 10. A method according to claim 9, in which the single atom thin film is one selected from the group consisting of Mo, Al, Cu, Ti, Ta, Pt, Ru, Rh, Ir, W, and Ag.
11. A method according to claim 9, in which the single atom oxide is one selected from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $\text{RuO}_2$ , and  $\text{IrO}_2$ .
- 20 12. A method according to claim 11, in which the refractive index of a film comprised of  $\text{Al}_2\text{O}_3$  is 1.67 to 1.73 in a wavelength range of 400 to 800 nm.
13. A method according to claim 9, in which the composite oxide is one selected from the group consisting of  $\text{SrTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{SrRuO}_3$ ,  $\text{CaRuO}_3$ ,  $(\text{Ba},\text{Sr})\text{TiO}_3$ ,  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ ,  $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ ,  $(\text{Sr},\text{Ca})\text{RuO}_3$ ,  $\text{In}_2\text{O}_3$  doped with Sn,  $\text{In}_2\text{O}_3$  doped with Fe, and  $\text{In}_2\text{O}_3$  doped with Zr.
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14. A method according to claim 9, in which the single atom nitride is one selected from the group consisting of SiN, NbN, ZrN, TaN,  $Y_3N_5$ , AlN, GaN, WN, and BN.
15. A method according to claim 9, in which the composite nitride is one selected from the group consisting of WBN, WSiN, TiSiN, TaSiN, AlSiN, and AlTiN.
- 5 16. A method of manufacturing a thin film substantially as shown in and/or described with reference to any of Figures 1 to 9, with or without reference to Figures 10 to 14.